



# Catalytic oxidation of heavy hydrocarbons over Pt/Al<sub>2</sub>O<sub>3</sub>. Influence of the structure of the molecule on its reactivity

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## ABSTRACT

Deep oxidation of 48 hydrocarbons (HCs), from 6 to 20 carbon atoms, was studied over a 1%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (105 m<sup>2</sup> g<sup>−1</sup>; mean particle size of Pt: 1 nm). The oxidation reaction (1500 ppm C of HC in air) was carried out by increasing the temperature by step of 5 °C from 100 to 400 °C. The reactivity of HCs was characterized by their *T*<sub>50</sub> (temperature at 50% conversion). The reactivity of *n*-alkanes increases with the chain length, following the same evolution with *n* as the ionization potential of the molecule. Isoalkanes are more difficult to oxidize than the corresponding *n*-alkanes. Hydrocarbon reactivity depends on the nature of carbon in the molecule. The ability to be oxidized is greater with C<sub>II</sub> and C<sub>III</sub> carbons while C<sub>I</sub> and C<sub>IV</sub> carbons, still more than C<sub>I</sub>, are refractory to oxidation. The reactivity of *n*-alkenes depends relatively little on the number of carbons in the molecule. Light alkenes are much more reactive than light alkanes while the reverse can be observed with long-chain hydrocarbons. Contrary to branched alkanes, isoalkenes or cyclenic hydrocarbons are generally more reactive than the corresponding *n*-alkenes. Short side-chain alkylbenzenes (toluene, ethylbenzene, ...) and polymethylbenzenes are more difficult to oxidize than benzene. When the length of the alkyl group is increased, the behaviour of the hydrocarbon in oxidation resembles more and more to long-chain alkanes with a better oxidability. Polyalkylbenzenes with hindered heavy alkyl groups are quite easy to oxidize. The behaviour of bicyclic or tricyclic hydrocarbons is much more complex. Partial or complete hydrogenation increases their reactivity. For instance, oxidability of bicyclic hydrocarbons is in the order: decaline > tetraline > naphthalene. The reactivity of heavier aromatics also depends on their ability to form partial oxidation intermediates (for instance: fluorene to fluorenone) or to possess extremely rigid internal C=C bonds (for instance: acenaphthylene and acenaphthene). These results were discussed in the light of several factors which can affect the reactivity in oxidation: (i) an electron transfer between adsorbed hydrocarbon and adsorbed oxygen species via the surface metal atoms; (ii) the mean C–H bond strength in the molecule and hindrance effects in branched hydrocarbons; (iii) the relative adsorption strength of oxygen and hydrocarbons; (iv) the relative reactivity of hydrocarbons and partially oxidized molecules, intermediates in total oxidation.

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## 1. Introduction

Heavy hydrocarbons, present as VOC in our environment, are emitted by various sources, mainly incomplete fuel combustion [1], asphalt transformation plants [2] and automotive engines [3–5]. They have a great impact on human health, most of these molecules provoking breathing diseases and cancers [6]. In automotive exhaust gases, they are generally emitted in gas phase or in condensed phase (aerosols) or in adsorbed phase on soot particulates [7]. Due to the high toxicity of heavy hydrocarbons, especially polycyclic aromatic hydrocarbons (PAHs), numerous

studies were performed to get a reliable speciation of these HCs, most often present at a sub-ppm level [8–12]. Heavy hydrocarbon emissions may largely vary depending on origin and nature of fuel [11,13,14], nature of vehicle [11,13,15], engine duty [16–18] and location of gas sampling [15,19]. A recent study also revealed the specific nature of hydrocarbons in transient cycle emissions [20]. A mean composition of heavy hydrocarbons and other organics present in Diesel exhaust gases or adsorbed on soots is given in Table 1. Catalytic oxidation of light alkanes, alkenes and aromatics were widely investigated over noble metal catalysts. Analysis of the pioneering works by Yu Yao [21,22] led to the following main conclusions [23]: (i) platinum is the most active metal in oxidation for virtually all the hydrocarbons except methane, for which palladium is preferred; (ii) light alkanes are difficult to oxidize: the higher the number of carbons in the molecule, the higher the

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**Table 1**

Mean chemical composition of hydrocarbons and other organics present in Diesel exhaust gases or adsorbed on soots. Total amounts: 30–100 ppm C.

Gaseous alkanes (C1–C40)	Aldehydes: <1 ppm C
CH <sub>4</sub> : 2–6 ppm C	Formaldehyde
C <sub>2</sub> H <sub>6</sub> : 2–5 ppm C	Acetaldehyde
C <sub>3</sub> +: 3–6 ppm C	Acroleine
Heavy alkanes (adsorbed on soots)	Propionaldehyde
nC16: 60 ppbC	Crotonaldehyde
nC17: 200 ppbC	Metacroleine
nC18: 380 ppbC	n-Butyraldehyde
nC19: 420 ppbC	Benzaldehyde
nC20: 320 ppbC	Naphthalenecarboxaldehyde
nC21: 230 ppbC	
nC22: 150 ppbC	
nC23: 50 ppbC	
Alkenes–dienes–alkynes	Ketones
Ethylene: 5–12 ppm C	Acetone
Acetylene: 3–9 ppm C	Xanthone
Propene: 2–4 ppm C	Fluorenone
Butenes < 1 ppm C	Alkylfluorenone
Butadiene: 1–2 ppm C	Acids
Pentenenes < 0.5 ppm C	Naphthalenic acid
	Acetic acid
	Benzoic acid
Light aromatics	Others (S and N compounds)
Benzene: 0.5–1 ppm C	Benzothiophene
Toluene: 0.5–1 ppm C	Dibenzothiophenes and
	alkyldibenzothiophenes: <0.5 ppm C
Ethylbenzene: <0.5 ppm C	Carbazole and methylcarbazoles
Xylenes: <0.5 ppm C	Nitro-PAH
PAH	Rest
Naphthalene: 1 ppbC	O <sub>2</sub> : 5–15%
Methyl-naphthalene: 3 ppbC	N <sub>2</sub> : 70–80%
Fluorene: 1 ppbC	CO <sub>2</sub> : 2–12%
Methyl-fluorenes: 10 ppbC	H <sub>2</sub> O: 1.8–10%
Phenanthrene: 10 ppbC	CO: 100–800 ppm
Methyl-phenanthrenes: 20 ppbC	H <sub>2</sub> : 30–300 ppm
Dimethyl-phenanthrenes: 3 ppbC	NO <sub>x</sub> : 30–600 ppm
Fluoranthene: 2 ppbC	SO <sub>2</sub> : 5–50 ppm
Pyrene: 1 ppbC	Particulates: 10–140 ppm C
Benzo[a]anthracene: <1 ppbC	
Benzo[b]fluoranthene: <1 ppbC	
Benzo[a]pyrene: <1 ppbC	

oxidation rate over Pt; (iii) alkenes, aromatics and alcohols are relatively easy to oxidize; (iv) light alkane oxidations are very sensitive to particle size of platinum, big particles being more active than small ones: for instance, turnover frequency in C<sub>3</sub>H<sub>8</sub> oxidation at 250 °C over Pt/Al<sub>2</sub>O<sub>3</sub> would increase from 0.16 s<sup>−1</sup> for 1 nm particles to 1.5 s<sup>−1</sup> for 12 nm particles and even to 10 s<sup>−1</sup> over Pt foil. In the last three decades, numerous studies were carried out confirming qualitatively these conclusions. The same ranking of activity was also obtained over commercial Pt-Rh/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> monolith catalysts under real conditions with CO, NO, H<sub>2</sub>O and CO<sub>2</sub> in the feed [24]. Light-off curves reported by these authors show that the temperatures for a 50% conversion were: methane, 515 °C > ethane, 435 °C > propane, 290 °C > hexane, 195 °C for alkanes, acetylene, 285 °C > ethylene, 205 °C > propene, 185 °C for alkene–alkynes, o-xylene, 225 °C > toluene, 220 °C > benzene, 205 °C for aromatics and n-butanol, 210 °C > n-propanol, 205 °C > ethanol, 200 °C > methanol, 195 °C for alcohols. General reviews on Volatile Organic Compounds (VOC) abatement confirmed Pt to be an excellent catalyst in VOC combustion [25,26]. Though oxidation of C1–C8 compounds was studied in detail, that of heavy hydrocarbons was more rarely investigated [27–29]. Heavy hydrocarbons were also studied as model compounds for the catalytic regeneration of particulate filters by fuel-borne catalysts like ceria [30,31] or for catalytic incinerators [32,33]. In these studies, naphthalene or methyl-1-naphthalene are generally used as model hydrocarbons of PAH [34,35]. The objective of this paper is to investigate the catalytic

oxidation of a great number of heavy hydrocarbons over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. These HCs were selected among those listed in Table 1, often detected in Diesel exhaust gases. For each family of hydrocarbons, a relationship between their molecular structure and their reactivity will be tentatively established.

## 2. Experimental

### 2.1. Catalyst

Most experiments were carried out on a 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by dry impregnation of a γ-alumina support with aqueous solution of hexachloroplatinic acid. The support (grain size: 2–4 mm; 105 m<sup>2</sup> g<sup>−1</sup>; pore volume: 1.18 cm<sup>3</sup> g<sup>−1</sup>) was crushed and sieved to 0.125–0.250 mm, calcined at 500 °C and impregnated with chlorhydric acid (2%) before Pt impregnation. This chlorination ensures a homogeneous distribution of Pt in the alumina grain. The chlorinated support was dried at 150 °C. Aliquot volume of concentrated solution of hexachloroplatinic acid (25 wt%) was diluted in the exact volume of water to fill in the pore volume. Preliminary tests showed that the pore volume of alumina (1.18 cm<sup>3</sup> g<sup>−1</sup>) could easily be filled with 0.9 cm<sup>3</sup> g<sup>−1</sup> of aqueous solution. After impregnation with hexachloroplatinic acid the catalyst was slowly dried in vacuum at 100 °C (10 h) and then at 150 °C (10 h). The solid was dechlorinated by washing with ammonia (0.1 M) and rinsed with pure water up to pH 7. It was dried again at 100–150 °C and calcined at 500 °C (2 h) and reduced in H<sub>2</sub> at 450 °C (2 h). No change of textural properties was noticed after Pt impregnation, drying, calcination and reduction. Chemical analyses led to the following composition (wt% or ppm): 0.99% Pt; 110 ppm K; 40 ppm Cl; 590 ppm Ca; 260 ppm Fe; 500 ppm Na and 300 ppm Si.

Platinum accessibility was measured by O<sub>2</sub>–H<sub>2</sub> titration at ambient temperature in a pulse chromatographic apparatus [36]. H/Pt<sub>5</sub> and O/Pt<sub>5</sub> stoichiometric ratios were supposed to be equal to unity. A dispersion of 80% was measured by this technique on the standard catalyst calcined at 500 °C and reduced in H<sub>2</sub> at 450 °C. Transmission electron microscopy showed that most Pt particles have a size below 1 nm. Some particles between 1 and 1.6 nm were seen on the TEM pictures. A mean particle size of 0.9–1 nm was calculated in agreement with H<sub>2</sub>–O<sub>2</sub> titration.

### 2.2. Hydrocarbons

About fifty hydrocarbons were selected to represent heavy HC emitted in Diesel exhausts. There may be distributed into three families: alkanes and isoalkanes, alkenes and isoalkenes, aromatics (mono- and polycyclic hydrocarbons). Some tests were also carried out over oxygenated compounds. Hydrocarbons were of purum grade for analysis (99% min) used without any further purification.

### 2.3. Oxidation reaction. Light-off measurements

The oxidation reaction was carried out in a flow reactor. The catalyst (0.035 g diluted in 2.7 g of α-Al<sub>2</sub>O<sub>3</sub>) was placed on a porous quartz disk. It was reduced in situ at 500 °C for 2 h in pure H<sub>2</sub> and cooled down to 100 °C in Ar. The hydrocarbon–air mixture was prepared by passing the flow of air (20 cm<sup>3</sup> min<sup>−1</sup>) in a vaporizer whose temperature T<sub>v</sub> was maintained constant at ±0.1 °C. T<sub>v</sub> was chosen between −25 and +120 °C so as to obtain a constant hydrocarbon pressure equivalent to 1500 ppm C (i.e. a molar concentration of 1500/n ppm, n being the carbon number in the molecule). The light-off curve was obtained by increasing the oven temperature by step of 5 °C from 100 to 400 °C. After stabilization of the temperature, at least two analyses were carried out and the decision to increase the temperature was taken as soon as the

conversion was constant. Each analyse taking about 8–10 min, the catalyst remains in the stationary state during 20 min at each plateau of temperature. It was verified that the metal kept a good dispersion after test. This is due to the relatively low temperature of oxidation (maximum 400 °C), to a moderate concentration of hydrocarbons and to the dilution of the catalyst in an inert material limiting hot spots. Moreover, the molar hydrocarbon concentration being adjusted to keep the same carbon concentration (1500 ppm C), the exothermicity is low and, if any, it is virtually the same for all the hydrocarbons.

Analyses were carried out on line by GC (column CPSil-5CB, 0.32 mm, 25 m) with a FID as detector. Identification of the possible intermediates was made by trapping the gases at –80 °C for further analyses on a GC–MS apparatus. The possible presence of CO in the products of total oxidation was checked in the conversion of some hydrocarbons (alkanes, aromatics). Carbon monoxide concentration was always below the detection limit of the analyzer (Dräger CO detector: 1 ppm).

The catalyst batch was stored after initial pre-reduction. This procedure was used to get a good platinum dispersion. Each catalyst sample was re-reduced and used for several oxidation tests (generally 10–12). It was not reduced between each light-off test. At the beginning and at the end of the series of light-off tests, toluene oxidation was systematically carried out for control. We found that the catalyst did not suffer any deactivation: light-off temperatures were the same on the fresh reduced catalyst and on the final “oxidized” catalyst.

### 3. Results

#### 3.1. Preliminary tests. Validity of the light-off temperature measurements

The reaction rate  $r$  ( $\text{mol s}^{-1} \text{g}^{-1}$ ) in a plug-flow reactor is given by:

$$r = -\frac{F}{mRT} \frac{dP}{dt} \quad (1)$$

where  $F$  is the volumic flow rate ( $\text{m}^3 \text{s}^{-1}$ ),  $m$ , the catalyst weight (g),  $R$ , the gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ),  $T$  the reaction temperature (K),  $P$  the partial pressure of hydrocarbon (Pa) and  $t$  the time (s).

The power-law kinetic equation can be written as:

$$-\frac{dP}{dt} = kP^n \quad (2)$$

where  $k$  is the rate constant and  $n$ , the kinetic order (with respect to HC).

In a differential reactor,  $\tau$ , the fractional conversion of HC is given by:

$$\tau = kP_0^{n-1} \delta \quad (3)$$

where  $\delta$  is the residence time in the catalytic bed and  $P_0$  is the inlet partial pressure of HC (considered as constant along the bed axis since  $\tau$  remains very low). The rate is then proportional to  $\tau$ :

$$r = \frac{FP_0}{mRT} \tau \quad (4)$$

In an integral reactor, a deviation arises between the rate calculated by Eq. (4) and the true reaction rate. To correct this deviation,  $\tau$  in Eq. (4) should be replaced by  $\tau^*$  given by [36]:

$$\begin{aligned} \tau^* &= \ln\left(\frac{1}{1-\tau}\right) \text{ for } n=1 \text{ or by } \tau^* \\ &= \frac{1}{n-1} \left[ (1-\tau)^{1-n} - 1 \right] \text{ for } n \neq 1. \end{aligned} \quad (5)$$

A first-order kinetics may be used to observe the deviation. An example is given in Fig. 1 for various hydrocarbons.

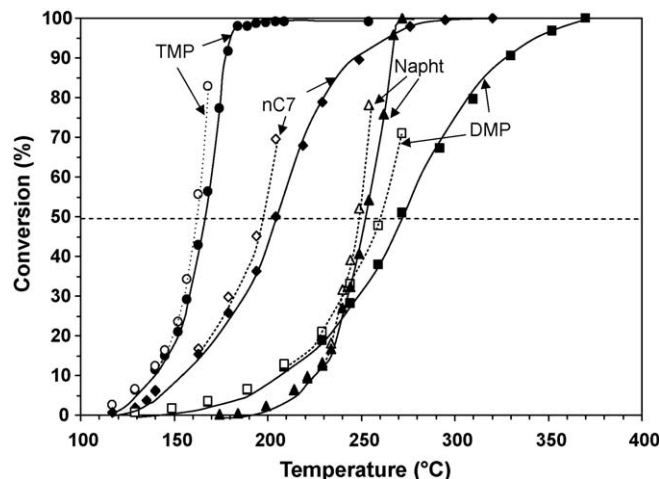


Fig. 1. Light-off curves of some hydrocarbons (full lines) and first-order transformations according to Eq. (5) (dotted lines). TMP, trimethyl-2,4,4-pent-2-ene; nC7, *n*-heptane; Napht, naphthalene; DMP, dimethyl-3,3-pentane. Reaction conditions: HC concentration: 1500 ppm C diluted in air; air flow rate:  $20 \text{ cm}^3 \text{min}^{-1}$ ; 35 mg catalyst.

Experimental conversions and first-order transformations plotted on the same graph show that the deviation observed for the light-off temperatures at 50% conversion ( $T_{50}$ ) are less than 12 °C and generally close to 5–6 °C for most hydrocarbons. It was not necessary to correct the data for comparing the  $T_{50}$  of the different hydrocarbons investigated in this study. Moreover, it was generally found that the Arrhenius plot determined with the 4–40% conversion points could be extrapolated up to 60–80% conversion. For a given class of hydrocarbons (for instance *n*-alkanes or *n*-alkenes or aromatics), their oxidability does not vary in the 0–50% interval of conversion, which validates the comparison at 50% conversion.

It was checked that there was no significant effect of  $\alpha\text{-Al}_2\text{O}_3$  and virtually no conversion in the empty reactor below 300 °C. An example is shown in Fig. 2 for naphthalene oxidation.

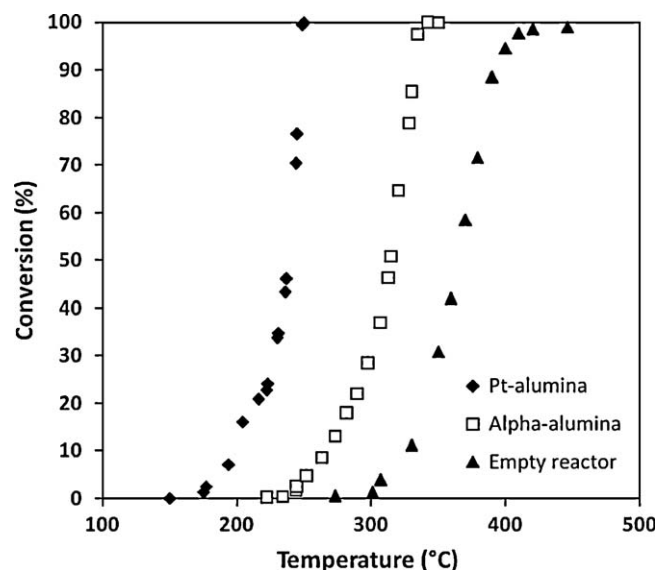


Fig. 2. Comparison of light-off curves of naphthalene over the 1 wt% Pt/ $\text{Al}_2\text{O}_3$  catalyst (0.035 g diluted in 2.7 g of  $\alpha\text{-Al}_2\text{O}_3$ ), over the diluent alone (2.7 g of  $\alpha\text{-Al}_2\text{O}_3$ ) and in the empty reactor.

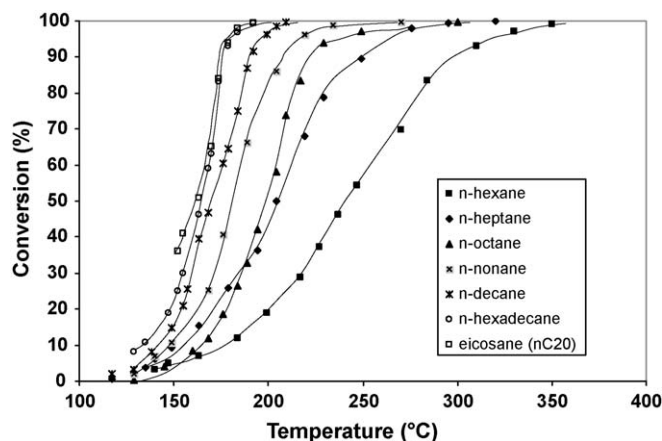


Fig. 3. Light-off curves of *n*-alkanes from C6 to C20. Same conditions as in Fig. 1.

### 3.2. Normal alkanes

Oxidation reactions were carried out on seven *n*-alkanes from C6 to C20. The light-off curves, presented in Fig. 3, clearly show that the hydrocarbon oxidability increases with the number of carbon in the molecule for values of *n* in between 6 and 10. For *n* > 10, light-off temperatures are very close and even virtually equal for *n* = 16 and *n* = 20. These results are coherent with previous works showing that oxidation rates of light alkanes can be ranked in the order:  $\text{CH}_4 > \text{C}_2\text{H}_6 > \text{C}_3\text{H}_8 > \text{C}_4\text{H}_{10} > \text{C}_6\text{H}_{14}$  [21,24,37].

### 3.3. Alkane isomers

Catalytic oxidation of a series of six C8 isomers was investigated and compared to C9 and C16 isomers. Light-off curves, presented in Fig. 4 (hexane isomers), Fig. 5 (octane isomers) and Fig. 6 (C9 and C16 isomers) show that there is a complex relationship between the degree of branching and the position of the alkyl groups with the oxidability of the HC molecule. The normal alkane is oxidized at the lowest temperature while certain isomers, specially those having quaternary carbons are extremely difficult to oxidize. For instance, the light-off temperature of dimethyl-2,2-butane is 69 °C higher than that

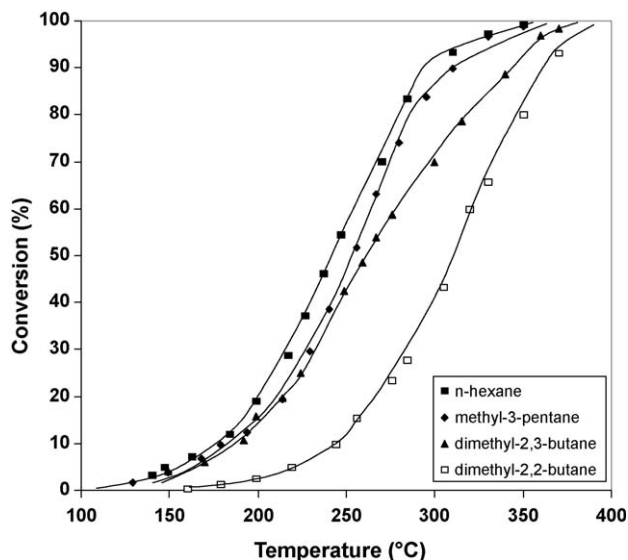


Fig. 4. Light-off curves of some C6 alkanes (*n*-C6 and isomers). Same conditions as in Fig. 1.

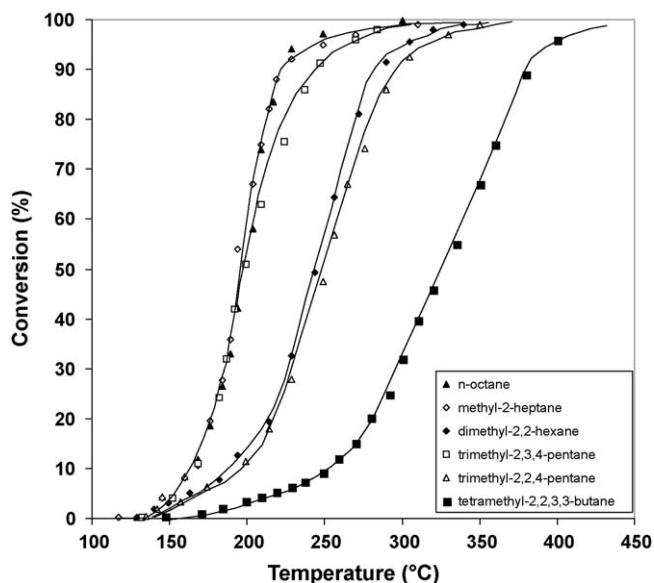


Fig. 5. Light-off curves of some C8 alkanes (*n*-C8 and isomers). Same conditions as in Fig. 1.

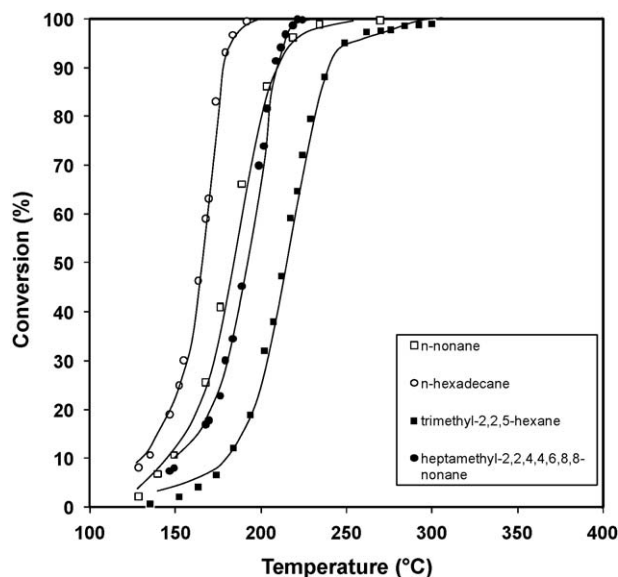


Fig. 6. Light-off curves of some C9 and C16 alkanes (*n*-C9, *n*-C16 and isomers). Same conditions as in Fig. 1.

of *n*-hexane (Fig. 4) while the light-off temperature of tetramethyl-2,2,3,3-butane is 120 °C higher than that of *n*-octane (Fig. 5). The relative oxidability of alkane isomers is thus correlated to the number of secondary, tertiary and quaternary carbons in the molecule. Data are reported in Table 2 and will be further discussed.


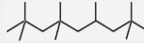

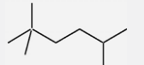
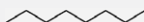
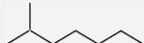
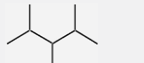
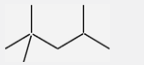
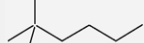
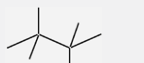

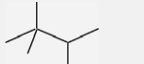
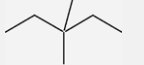

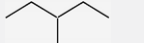
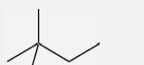
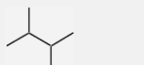
### 3.4. Normal alkenes and cyclohexene

Light-off curves of  $\text{C}_7$ – $\text{C}_{10}$  normal alkenes and cyclohexene are reported in Fig. 7. The oxidation behaviour of *n*-alkenes virtually does not depend on the chain length ( $T_{50} = 198 \pm 2$  °C). Moreover, the light-off temperature of  $\text{C}_7$ – $\text{C}_{10}$  normal alkenes is extremely close to that of cyclohexene (196 °C). These results contrast with those obtained with *n*-alkanes whose  $T_{50}$  values decrease with the chain length. This makes that  $\text{C}_6$  and  $\text{C}_7$  alkenes are more reactive than corresponding alkanes while for  $n \geq 8$ , *n*-alkanes are oxidized at lower temperatures



**Table 2**

Structure–reactivity relationship in alkane isomers oxidation.

Formula	Hydrocarbon	Number of carbon atom	$T_{50}$ (°C)	Number of carbon atoms	
				Primary C <sub>I</sub> Secondary C <sub>II</sub>	Tertiary C <sub>III</sub> Quaternary C <sub>IV</sub>
	<i>n</i> -Hexadecane	16	165	2 14	0 0
	Heptamethyl-2,2,4,4,6,8,8-nonane	16	192	9 3	1 3
	<i>n</i> -Nonane	9	183	2 7	0 0
	Trimethyl-2,2,5-hexane	9	211	5 2	1 1
	<i>n</i> -Octane	8	202	2 6	0 0
	Methyl-2-heptane	8	195	3 4	1 0
	Trimethyl-2,3,4-pentane	8	197	5 0	3 0
	Trimethyl-2,2,4-pentane	8	250	5 1	1 1
	Dimethyl-2,2-hexane	8	245	4 3	0 1
	Tetramethyl-2,2,3,3-butane	8	322	6 0	0 2
	<i>n</i> -Heptane	7	204	2 5	0 0
	Trimethyl-2,2,3-butane	7	262	5 0	1 1
	Dimethyl-3,3-pentane	7	272	4 2	0 1
	<i>n</i> -Hexane	6	243	2 4	0 0
	Methyl-3-pentane	6	254	3 2	1 0
	Dimethyl-2,2-butane	6	312	4 1	0 1
	Dimethyl-2,3-butane	6	260	4 0	2 0

than *n*-alkenes. Though oxidation of long-chain alkenes ( $n > 7$ ) is not sensitive to the chain length, it seems that the number of carbon may affect the reactivity of light *n*-alkenes. For instance, Bart et al. showed that propene was more reactive than ethylene over Pt-Rh catalysts ( $\Delta T_{50} = 20$  °C in similar conditions than ours) [24].

### 3.5. Alkene isomers

Light-off curves of different isomers of C<sub>6</sub>–C<sub>8</sub> alkenes are reported in Fig. 8. The curve of *n*-octene is also shown for purpose of comparison. The selected isomers present a high degree of substitution on the sp<sup>2</sup> carbon of the double bond. Contrary to alkane isomers, these alkene isomers are more reactive than the corresponding *n*-alkenes (Fig. 8 and Table 3). In the case of dimethyl-2,2-but-2-ene (four methyl substituents on the double bond), of trimethyl-2,3,3-but-1-ene (one methyl substituent and

one tertibutyl substituent in *gem* position), of trimethyl-2,4,4-pent-2-ene (two methyl substituents in *gem* position and one tertibutyl substituent), light-off temperatures are in between 160 and 166 °C, i.e. 40 °C lower than those of the linear alkenes. In the case of trimethyl-2,4,4-pent-1-ene (one methyl in *gem* position and one relatively big alkyl group substituent), light-off temperature is somewhat higher (176 °C) though still lower than the C<sub>8</sub> *n*-alkene.

### 3.6. Dienes

Oxidation of octa-1,5-diene and octa-1,7-diene were compared to that of oct-1-ene. Light-off curves (not reported) show that the dienes oxidize at a temperature slightly higher than that of *n*-alkene ( $T_{50} = 201$  °C for oct-1-ene, 208 °C for octa-1,5-diene and 211 °C for octa-1,7-diene). There is little effect of the presence of a second double bond in the molecule.

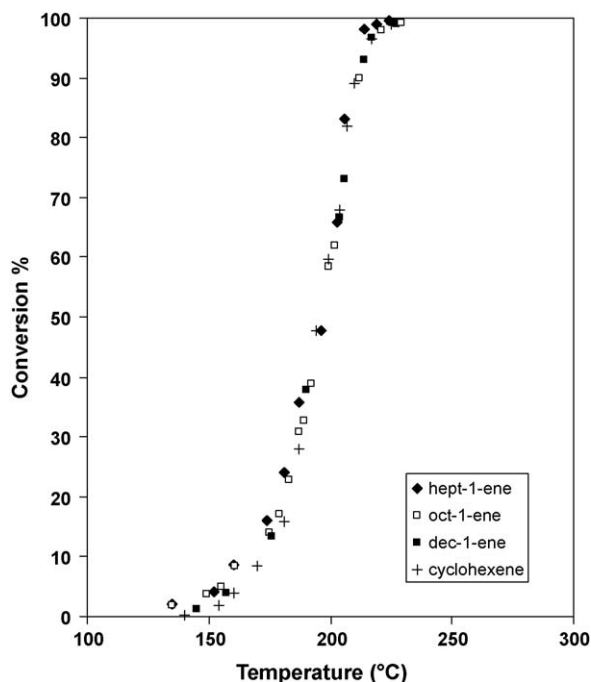


Fig. 7. Light-off curves of C7–C10 *n*-alkenes and cyclohexene. Same conditions as in Fig. 1.

### 3.7. Monocyclic aromatics

Light-off curves of benzene and selected alkyl- or polyalkylbenzenes are compared in Fig. 9. The effect of the chain length in *n*-alkylbenzenes  $C_6H_5-C_nH_{2n+1}$ , with  $0 < n < 10$ , is shown in Fig. 9a. As a rule, *n*-alkylbenzenes are more difficult to oxidize than benzene. Oxidability decreases in the order ( $T_{50}$  in parentheses): benzene (191 °C) > toluene (216 °C) > ethylbenzene (227 °C)  $\approx$  *n*-butylbenzene (228 °C). However, for

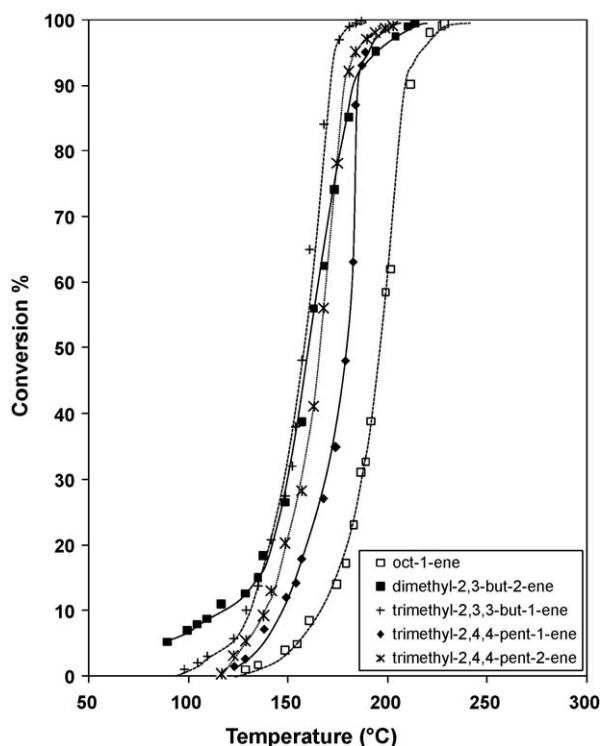


Fig. 8. Light-off curves of some C6, C7 and C8 alkenes. Same conditions as in Fig. 1.

Table 3

Structure–reactivity relationship in alkene isomers.

Formula	Name	$T_{50}$ (°C)
	Dimethyl-2,2-but-2-ene	162
	Trimethyl-2,3,3-but-1-ene	160
	Trimethyl-2,4,4-pent-2-ene	166
	Trimethyl-2,4,4-pent-1-ene	176

longer chains as in *n*-decylbenzene (195 °C), the oxidability increases again and becomes virtually equal to that of benzene. A similar trend can be observed in polymethylbenzene oxidation (Fig. 9b): the light-off temperature is minimum for benzene and maximum for toluene. When the number of methyl groups is increased,  $T_{50}$  decreases and becomes closer and closer to that of benzene (196 °C for hexamethylbenzene). A surprising effect can be observed in the oxidation of benzene substituted with hindered alkyl or polyalkyl groups (Fig. 9c). While linear alkyl groups confer to substituted benzenes a less good oxidability (at the best equal to that of benzene), hindered, branched alkyl groups can make polyalkylbenzenes much more reactive ( $T_{50}$  = 176 °C for ditertio-butylbenzene).

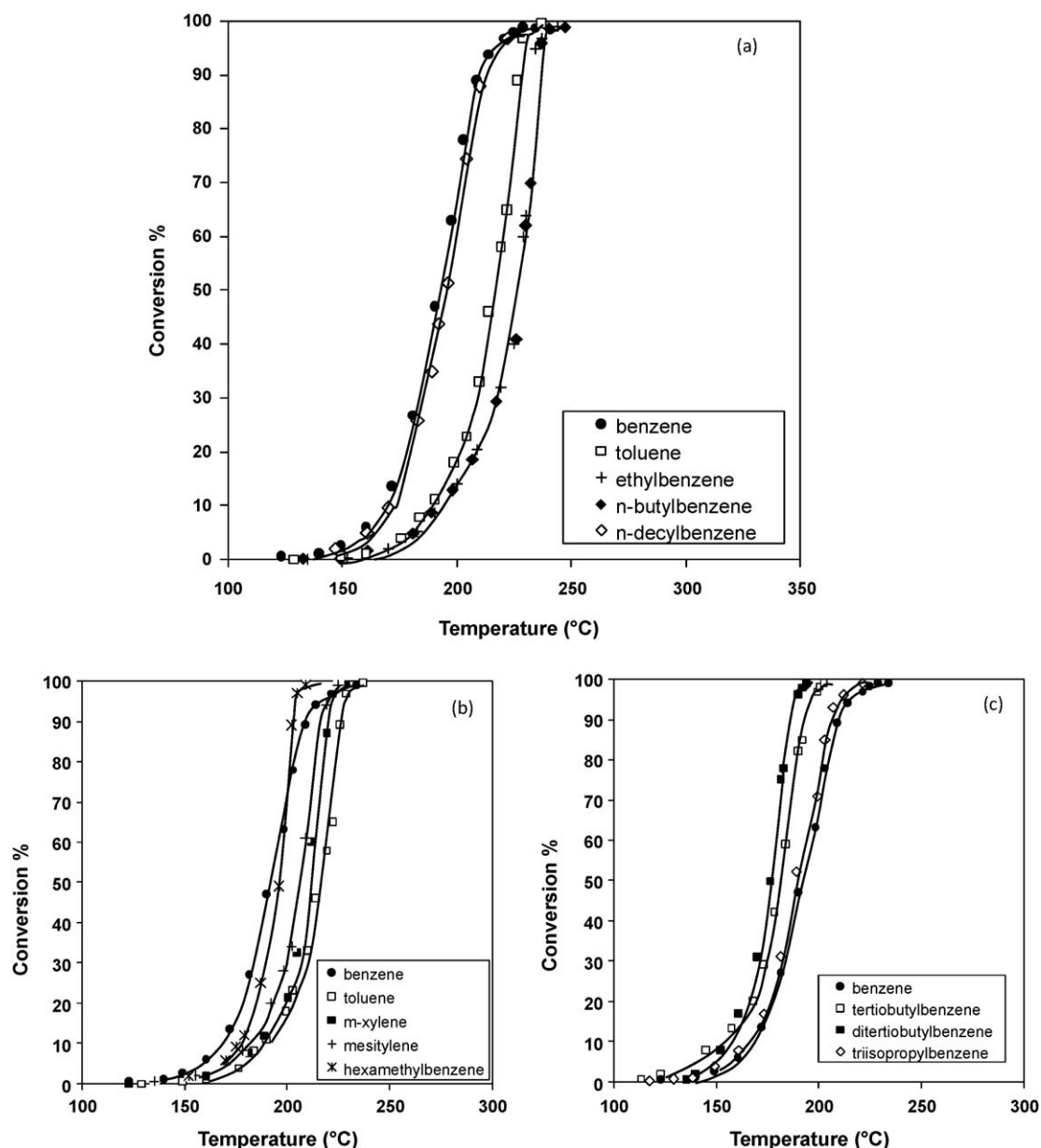
Benzene oxidizes at much lower temperature than *n*-hexane ( $T_{50}$  = 242 °C, i.e.  $\Delta T_{50}$  = 51 °C). This is an exceptional behaviour, all the *n*-alkylbenzenes oxidizing at higher temperature than the *n*-alkanes having the same number of carbon atoms:  $\Delta T_{50}$  = 12 °C, 28 °C and 58 °C for C7, C8 and C10 hydrocarbons, respectively.

### 3.8. Polycyclic hydrocarbons

Light-off temperatures of selected polycyclic hydrocarbons are reported in Table 4. As oxygenated derivatives of these hydrocarbons are possible intermediates in oxidation, some of them (1,4-naphthoquinone, phthalic anhydride, 9-fluorenone) were also investigated. Due to its very low volatility, the oxidation of phenanthrene could not be evaluated in the reactor used in this study.

Naphthalene ( $T_{50}$  = 240 °C) is much less reactive than *n*-decane ( $T_{50}$  = 171 °C), which shows that the stabilization of the aromatic rings tends to inhibit their oxidation. Decreasing the aromaticity by partial hydrogenation (tetraline,  $T_{50}$  = 230 °C) or by total hydrogenation (decaline,  $T_{50}$  = 205 °C) largely suppresses this inhibiting effect, even if cyclanic hydrocarbons remain less reactive than linear ones. Hydrogenated polycyclic hydrocarbons being less toxic than the corresponding PAHs, some authors proposed to reduce toxicity by catalytic hydrogenation [38,39].

A possible step in the total oxidation of polycyclic hydrocarbons is the formation of oxygenated intermediates. Naphthoquinones, specially 1,4-naphthoquinone, and phthalic anhydride are known to be easily formed by partial oxidation of naphthalene over certain transition metal oxide catalysts such as  $V_2O_5$  [40]. Table 4 reveals



**Fig. 9.** Light-off curves of benzene and selected alkylbenzenes: (a) *n*-alkylbenzenes  $C_6H_5-C_nH_{2n+1}$ , with  $0 < n < 10$ ; (b) polymethylbenzenes  $C_6H_5(CH_3)_n$  with  $0 < n < 6$ ; (c) hindered alkyl or polyalkyl substituted benzene.

that these oxygenated compounds have behaviour in oxidation not very different to that of naphthalene: they are only slightly more reactive and oxidize at about 10–15 °C below the light-off temperature of naphthalene. The formation of naphthoquinones and phthalic anhydride does not seem to be a crucial step in the total oxidation of naphthalene.

A comparison of perhydrophenanthrene ( $T_{50} = 215$  °C) and 9,10-dihydrophenanthrene ( $T_{50} = 245$  °C) confirms that hydrogenation of the aromatic ring increases significantly its oxidability.

The case of fluorene is quite different. A detailed analysis of the products of reaction showed that fluorenone is the major oxidation product even at very high fluorene conversion (Fig. 10). Between 197 °C (light-off temperature of fluorene) and 222 °C (light-off temperature of 9-fluorenone), fluorene is essentially transformed into fluorenone and not into  $CO_2$ . If one takes into account the yield of  $CO_2$ , the light-off curve of fluorene becomes very close to that of 9-fluorenone: the true light-off temperature of fluorene in the total oxidation reaction is close to 220 °C.

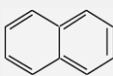
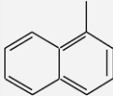
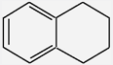
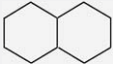
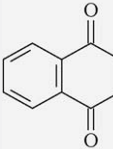
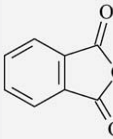


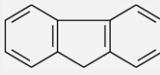
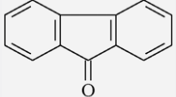
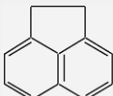
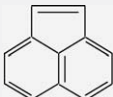
The behaviour of acenaphthene in oxidation is very similar to that of naphthalene ( $T_{50} = 243$  and 240 °C, respectively). The presence of a C5 cycle condensed on the aromatic naphthalene ring does not change its reactivity. By contrast, acenaphthylene is more difficult to oxidize ( $T_{50} = 255$  °C). The presence of the C=C bond in the C5 cycle reinforce the global tightness of the tricyclic molecule and decreases the carbon reactivity in oxidation. Acenaphthene oxidation produces a significant amount of acenaphthylene (Fig. 11). However, the selectivity to acenaphthylene decreases rapidly with acenaphthene conversion so that the true light-off temperature of acenaphthene remains close to 243 °C.

## 4. Discussion

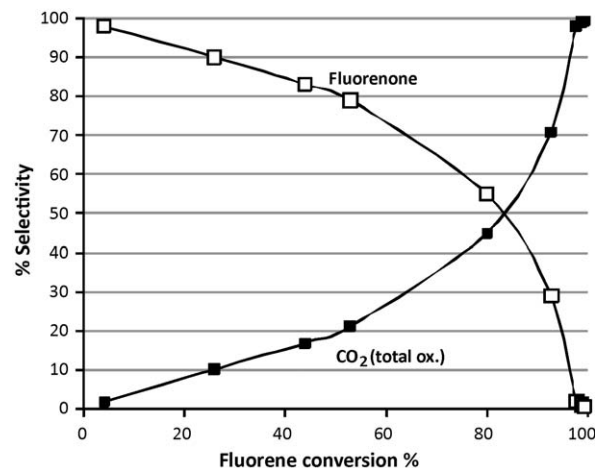
### 4.1. Structure–reactivity relationships in alkane oxidation

It is generally admitted that the C–H bond cleavage is a key factor for alkane catalytic oxidation [41]. C–H bonds are relatively strong in

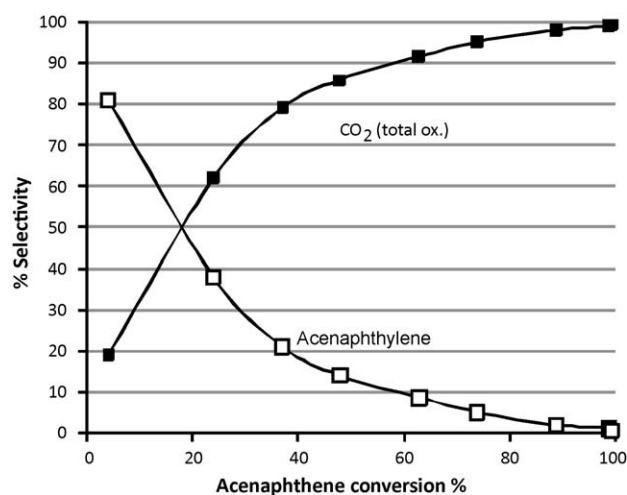
**Table 4**  
Structure–reactivity relationship in polycyclic hydrocarbons.

Formula	Name	$T_{50}$ (°C)
	Naphthalene	240
	Methyl-1-naphthalene	238
	Tetraline	230
	Decaline	205
	1,4-Naphthoquinone	221
	Phthalic anhydride	218
	Perhydrophenanthrene	215
	9,10-Dihydrophenanthrene	245
	Fluorene	197
	9-Fluorenone	222
	Acenaphthene	243
	Acenaphthylene	255

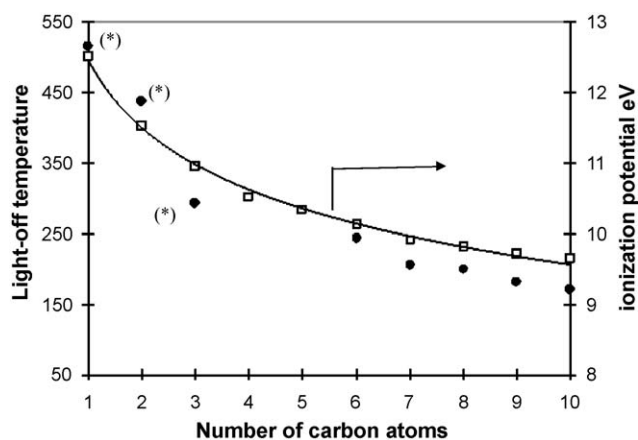
light alkanes, which makes the alkyl–platinum bond formation less easy than in long-chain alkanes. Oxygen adsorbs on the catalyst surface to give highly reactive anionic species  $O^-$  and  $O_2^-$ . While superoxides can be formed upon  $O_2$  adsorption over metal oxides and zeolites [42–44], mononuclear anions  $O^-$  are preferably formed on metal surfaces. Disappearance potential spectroscopy (DAPS) clearly showed an electron transfer from Pt to adsorbed O species with peaks close to the first ionization potential of platinum [45]. Electrons could be given via the Pt surface by adsorbed hydrocarbons according to the Franck-Condon principle on electronic transitions



**Fig. 10.** Selectivity to fluorenone and to  $CO_2$  (total oxidation) in fluorene oxidation.



**Fig. 11.** Selectivity to acenaphthylene and to  $CO_2$  (total oxidation) in acenaphthene oxidation.



**Fig. 12.** Correlation between the light-off temperatures of  $n$ -alkanes and their ionization potential. Black circles:  $T_{50}$  values (°C) values for C1–C3 alkanes are taken from Ref. [37]); open squares: ionization potential in eV.



(no change in the nuclear configuration). Hydrocarbon ionization can be described by the following reaction:



The following step of oxidation would be the reaction between the radical cation  $R^{\bullet+}$  and the surface oxygen species. Fig. 12 shows that there is a good correlation between the light-off temperatures of *n*-alkanes and their ionization potential [46], which supports the oxidation mechanism by an electron transfer between adsorbed hydrocarbon species and adsorbed oxygen species via the metal surface. The curve of Fig. 12 can be fitted using the following relationship for  $6 < n < 20$ :

$$T_{50}(n) = 165 + 11.1 \left( \frac{16}{n-4} - 1 \right) \quad (7)$$

where  $T_{50}(n)$  is the light-off temperature (°C) of the *n*-alkane and 165 is the light-off temperature of eicosane (*n*-alkane with 20 carbon atoms).

There are many indications in the literature that the C–H bond cleavage is a determining step of alkane oxidation reactions. This has been proven and discussed in detail by Hodnett et al. for partial oxidation reactions [47–49]. These authors collected a great number of literature data in alkane oxydehydrogenation (ODH) or in alkane ammoxidation and showed that the product yield was well-correlated with the weakest C–H bond energy both in the alkane and the product (alkenes, nitriles). From a detailed kinetic study of ODH of several alkanes over VOx–Al<sub>2</sub>O<sub>3</sub>, Zboray et al. showed that the initial step of reaction depended from the C–H bond activation, all the C–H bonds of the molecule being potential candidates for activation [50]. Zboray et al. concluded that the apparent activation energy was a rate-weighted average over all C–H bonds in the molecule, not only the weakest C–H bond as in the model of Hodnett et al. Finally, Zboray et al. suggested that alkane ODH and alkane combustion proceeded via the same intermediate species, an alkoxide issued from the C–H bond splitting. From this study, one may infer that the structure–reactivity relationship in alkane ODH may be extended to alkane combustion. A close examination of the light-off temperatures of several normal and branched alkanes shows that there is no correlation between the reactivity and the ionization potential of the hydrocarbons (Table 5). In isoalkane series, the oxidation reaction is not governed by the electronic transfer between adsorbed hydrocarbons and adsorbed oxygen species. A likely hypothesis is that the C–H bond cleavage becomes the slow step of reaction. Following the concept of Zboray et al. [50], one may postulate that the reactivity is a mean contribution of all the C–H bonds of the hydrocarbon molecule, with a prominent role of the weakest C–H bond. The light-off temperature can then be fitted by a linear relationship:

$$T_{50} = T_{50}(n) + aC_I + bC_{II} + cC_{III} + dC_{IV} \quad (8)$$

where  $C_X$  represents the number of carbon atoms of type X.

The data reported in Table 2 show that alkane reactivity slightly depends on the number of  $C_{II}$  and  $C_{III}$  (positive effect on the reactivity, i.e. a decrease of  $T_{50}$ ), fairly on the number of  $C_I$  atoms and strongly on the number of  $C_{IV}$  atoms (negative effect on the reactivity, i.e. an increase of  $T_{50}$ ). This means that (i)  $a$  and  $d$  are positive with  $d > a$  and (ii)  $b$  and  $c$  are negative and smaller than  $a$  and  $d$  in absolute values. It can also be seen on Table 2 that the moderate effects of  $C_{II}$  and  $C_{III}$  atoms cannot be discriminated so that  $b \approx c$ . Moreover, the effect of the presence of one  $C_{IV}$  atoms is less dramatic on longer chains than on the shorter ones. For that reason, it is assumed that the coefficient  $d$  depends on  $n$ . The best fit leads to the following relationship for  $7 < n < 16$ :

$$T_{50} = T_{50}(n) + 2.9C_I - 1.5(C_{II} + C_{III}) + 55.5 \left( \frac{C_{IV}}{n - C_{IV} - 5} \right) \quad (9)$$

**Table 5**

Light-off temperatures and ionization potential of several *n*- and isoalkanes.

Hydrocarbon	$T_{50}$ (°C)	Ionization potential (eV)
<i>n</i> -Hexane	243	10.13
Methyl-3-pentane	254	10.08
Dimethyl-2,3-butane	260	10.02
Dimethyl-2,2-butane	312	10.06
<i>n</i> -Octane	202	9.82
Methyl-2-heptane	195	9.84
Trimethyl-2,2,4-pentane	250	9.86
Tetramethyl-2,2,3,3-butane	322	9.80

This equation remains valid for  $n = 6$  by replacing  $n - C_{IV} - 5$  by  $n - C_{IV} - 4$  for the compound containing a  $C_{IV}$  carbon (dimethyl-2,2-butane). Applied to compounds of Table 2, Eq. (9) gives a maximal deviation of 19 °C for dimethyl-2,3-butane (241 °C instead of 260 °C) and the exact value for methyl-2-heptane and tetramethyl-2,2,3,3-butane. The mean deviation is close to 4 °C. This model based on the number of  $C_I$ – $C_{IV}$  carbon atoms could probably be improved by considering the environment of each atom. Detailed studies on hydrogenolysis of branched alkanes showed that  $C_A$ – $C_B$  bond scission in a  $C_A$ – $C_B$ – $C_X$  chain strongly depends on the nature of  $C_X$  (tertiary or quaternary) [51]. These changes in the C–C bond strength depending on the nature of the surrounding carbons should obviously affect their reactivity in oxidation.

#### 4.2. Structure–reactivity relationships in alkene, isoalkene and diene oxidation

Contrary to alkanes, alkene adsorption on Pt does not require a preliminary C–H bond cleavage. Alkenes can adsorb via  $\pi$ -bonding between the C=C bond and the platinum atoms [52–55]. The second step is the transformation of this  $\pi$ -coordinated alkene–Pt species into a di- $\sigma$  species which leads to C–C bond scission and reaction with adsorbed oxygen. Analysis of data of Yu Yao [21,22] shows that alkenes are generally adsorbed more strongly than oxygen on Pt: negative orders in alkene and positive orders in oxygen are observed. The results of Fig. 6 show that *n*-alkene or cyclohexene oxidation is virtually insensitive to the chain length for  $7 < n < 10$  or to cyclisation. Oxidation of light alkenes (ethylene to *n*-hexene) was studied by Amon-Meziere et al. who showed that light-off temperatures slightly increased with the chain length [56]. The reverse effect was observed on *n*-alkanes but contrary to this class of hydrocarbons, the influence of the chain length is very weak. A possible explanation is that the slow step of reaction is the C=C bond rupture, whose strength depends little on the chain length.

Isoalkenes are much more reactive than *n*-alkenes. Again, the tendency is the reverse of that of alkanes and isoalkanes. The most probable explanation is that isoalkenes are less strongly adsorbed than *n*-alkenes. For instance, Tsai et al. reported that the adsorption heat of ethylene on Pt(1 1 1) decreases when hydrogen atoms in the CH<sub>2</sub>=CH<sub>2</sub> molecule were successively replaced by methyl groups [57]. Increasing the alkene branching should decrease auto-inhibition (negative order in alkene) and thus increase the reactivity in oxidation. The reverse can be observed with dienes, more strongly adsorbed than monoenes.

#### 4.3. Structure–reactivity relationships in aromatics oxidation

Elimination of benzene from gaseous effluents has received a great attention in reason of its toxicity. Dryakhlov et al. were among the first authors to investigate the combustion of benzene over Pt catalysts [58–60]. They concluded that benzene

was converted by a heterogeneous–homogeneous mechanism with certain steps occurring in gas phase. For environmental reasons, catalytic oxidation of aromatics has recently gained more and more interest. Benzene and toluene oxidations were investigated by several authors over Pt catalysts [61–63]. It was observed that toluene oxidized at higher temperature than benzene in the concentration range close to that of the present study. At lower concentration, light-off temperatures of benzene and toluene tend to become very close [61]. Aromatic hydrocarbons can be strongly adsorbed on platinum surface. Competitive hydrogenation of benzene and toluene revealed that toluene was more strongly bonded to metal surfaces than benzene [64] with the possibility to form H-deficient adsorbed intermediates [65]. Some side reactions can also occur with toluene, such as selective oxidation to benzaldehyde. This reaction is so easy that it was shown to occur over alumina [66]. When the length of the alkyl group increases, the alkylbenzene reactivity first decreases and then re-increases for longer alkyl group chains. Apparently the lower reactivity of alkylbenzenes is balanced by the higher oxidability of long-chain alkanes. There is very few information on the adsorption mode of these aromatics on platinum. One may infer that the molecule adsorbs both via the aromatic ring and the alkyl group, the behaviour in oxidation being then comparable to a mixture of benzene and alkanes or alkenes.

Several factors may govern the reactivity of polycyclic hydrocarbons: (i) the loss of aromaticity (partially or fully hydrogenated compounds are more reactive than the starting aromatic molecule) and (ii) the propensity of the bicyclic aromatics to give selective oxidation compounds which are intermediate in total oxidation. For these heavy aromatics, it is necessary to have a detailed analysis of all the intermediates to understand their reactivity.

#### 4.4. Particle size effects

The catalyst used throughout this study is a well-dispersed Pt catalyst (around 1 nm). Oxidation reactions (especially in the alkane series) may be very sensitive to particle sizes of platinum. For instance, oxidation of light alkanes is much easier on big platinum particles [22]. It was shown that O<sub>2</sub> activation (adsorption/desorption and dissociation) was also much easier on 5–10 nm Pt particles than on 1–2 nm ones [67] and there is no doubt that HC activation can also depend on the surface structure of platinum and thus on the particle size [68]. It was verified that Pt keeps a good dispersion in the light-off tests: all the results presented in this study reflect the behaviour of small particles of platinum. Investigations are in progress to evaluate the changes in hydrocarbon reactivity on bigger particles of platinum.

## 5. Conclusions

From this study, several conclusions can be drawn on the reactivity of hydrocarbons in oxidation over Pt:

- It is confirmed that the reactivity of *n*-alkanes increases with the number of carbons in the molecule up to *n* = 20 (eicosane). There is a good correlation between the light-off temperature (*T*<sub>50</sub>) and the ionization potential, both following the same evolution with the number of carbons in the molecule.
- Isoalkanes are less reactive than *n*-alkanes, particularly those containing quaternary carbons. Light-off temperatures of isoalkanes is a function of nature and number of carbons in the molecules, whose reactivity vary as follows: C<sub>II</sub> ≈ C<sub>III</sub> > C<sub>I</sub> >> C<sub>IV</sub>.

- The reactivity of *n*-alkenes depends little on the number of carbons in the molecule. Light alkenes are more reactive than light alkanes while the reverse is true for heavier hydrocarbons. Whatever the size of the molecule, the alkene would be strongly adsorbed on the platinum surface.
- Contrary to alkanes, branched alkenes are more reactive than the corresponding *n*-alkenes. The presence of more or less big substituents on the C=C bond might decrease the strong interaction between the unsaturated compound and the metal surface.
- The oxidability of alkylbenzenes depends on the alkyl group length. It decreases for aromatics bearing short alkyl groups: ethylbenzene and toluene are less reactive than benzene. The reverse tendency is observed for longer or hindered alkyl groups. The reactivity becomes close to that of long-chain alkanes.
- The reactivity of bicyclic or tricyclic compounds is complex. Partial or perhydrogenation of the cycles increases their reactivity. The reactivity of bicyclic compounds is as follows: decaline > tetraline > naphthalene. Other factors may influence the total oxidation reaction: the ability of polycyclic hydrocarbons to form partially oxidized intermediates (for instance: fluorene to fluorenone) or to possess rigid C=C bond in the molecule (acenaphthylene is very difficult to oxidize).

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